Microstructural Stability of 9-12%Cr Steels at Elevated Temperatures

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9-12 Cr Steels

- Various martensitic 9-12 Cr steels are utilized in advanced energy plants for their good elevated temperature properties:
  - Creep strength
  - Steam side oxidation resistance
  - Fire side corrosion resistance
  - Thermal fatigue resistance

Applications

- **Boilers:**
  - Superheater tubing
  - Headers
  - Steam pipes
- **Steam Turbines:**
  - Rotors
  - Casings
  - Valves
  - Inlet pipes

Motivation for Current Research

- Need for further improvements on the properties for higher temperature (>600°C) use driven by the environmental concerns (i.e., improve efficiency to reduce emissions and fossil fuel consumption)

Objective

- Explore new subsitutional solute solution (Cu, Co) and precipitate (TiC) hardening mechanisms for improved strength of 9-12 Cr martensitic steels

Alloy Design

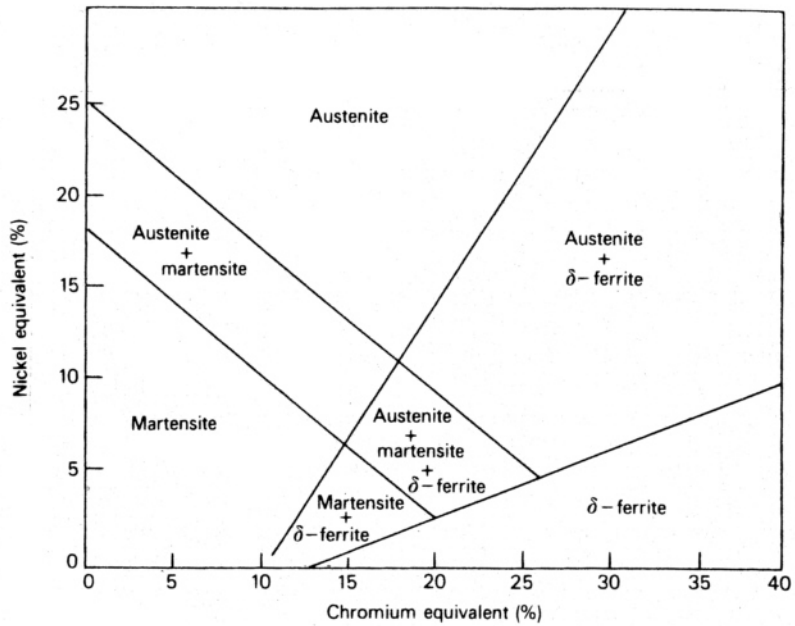
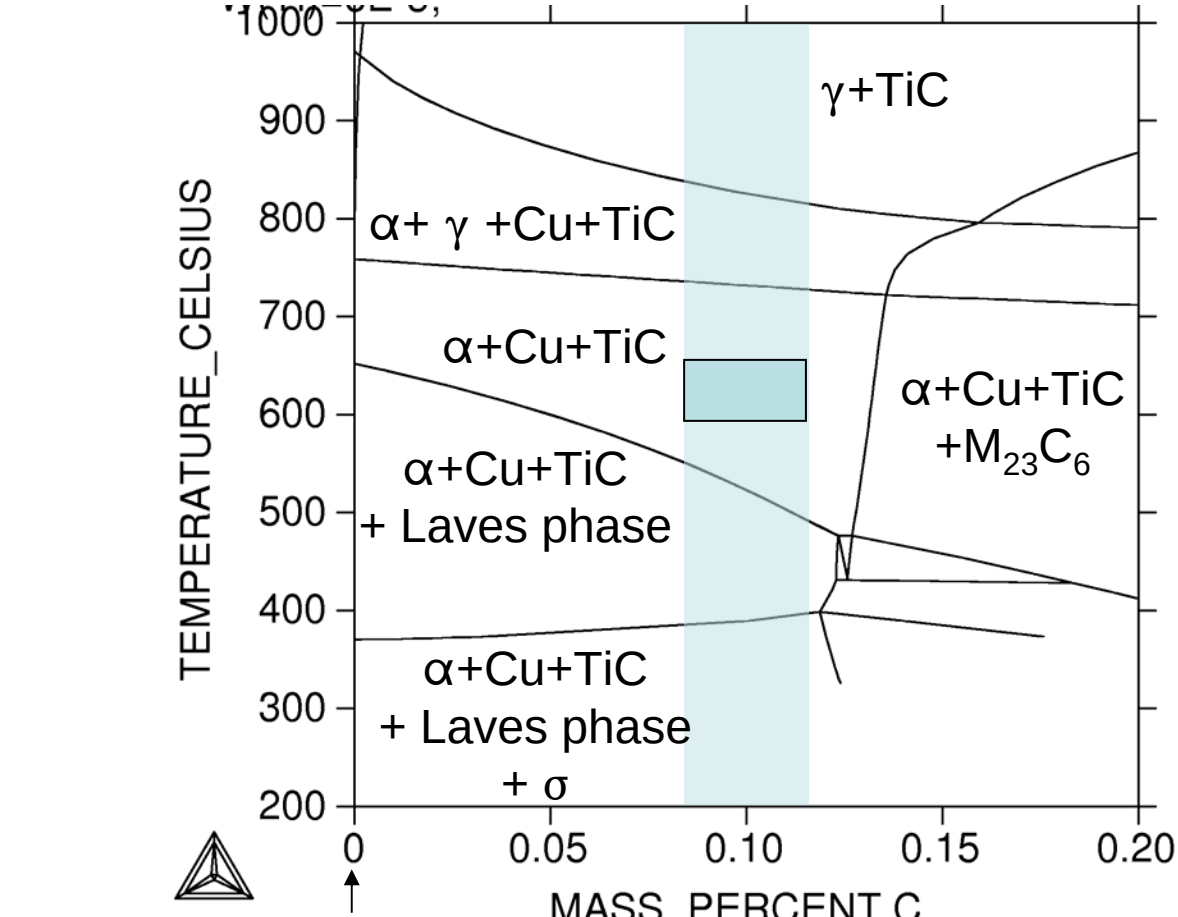


Fig. 12.4 Schaeffler diagram. Effect of alloying elements on the basic structure of Cr–Ni stainless steels (Schneider and Climax Molybdenum Co., *Foundry Trade J.* **108,** 562, 1960).

Nominal Composition of Alloys (wt%)

Alloy	Fe	Cr	Cu	Co	Mo	Ni	Ti	C	Mn	Si	Other
HR52	**Bal**	**9**	**3**	**3**	**0.7**	**1**	**0.5**	**0.1**	**-**	**-**	
HR53	**Bal**	**10.5**	**3**	**4**	**0.7**	**1**	**0.5**	**0.1**	**-**	**-**	
HR54	**Bal**	**12**	**3**	**4**	**0.7**	**1**	**0.5**	**0.1**	**-**	**-**	
HR58	**Bal**	**9**	**3**	**3**	**0.7**	**1**	**0.5**	**0.1**	**-**	**0.25**	
HR59	**Bal**	**9**	**3**	**3**	**0.7**	**1**	**0.5**	**0.1**	**0.2**	**0.25**	
HR60	**Bal**	**9**	**3**	**3**	**0.7**	**1**	**0.5**	**0.1**	**0.6**	**0.25**	
HR61	**Bal**	**9**	**3**	**3**	**0.7**	**1**	**0.5**	**0.1**	**1**	**0.25**	
P91	**Bal**	**9**	**0.1**	**-**	**1**	**0.3**	**-**	**0.1**	**0.5**	**0.3**	**0.2V-0.08Nb**

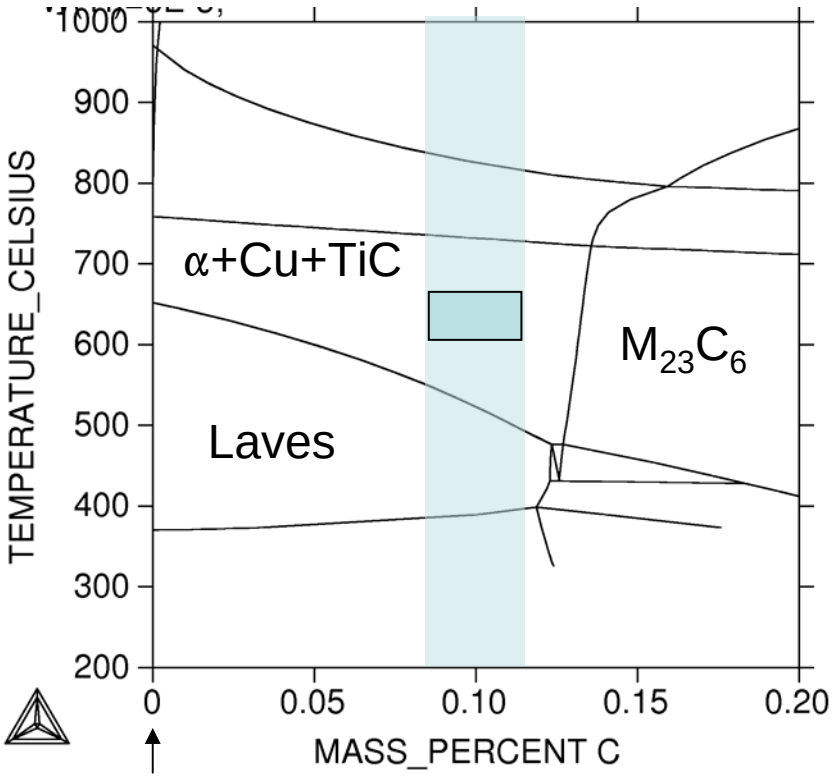
Thermodynamic calculation of phases in HR52



Fe-9Cr-3Cu-3Co-1Ni-0.7Mo-0.6Ti

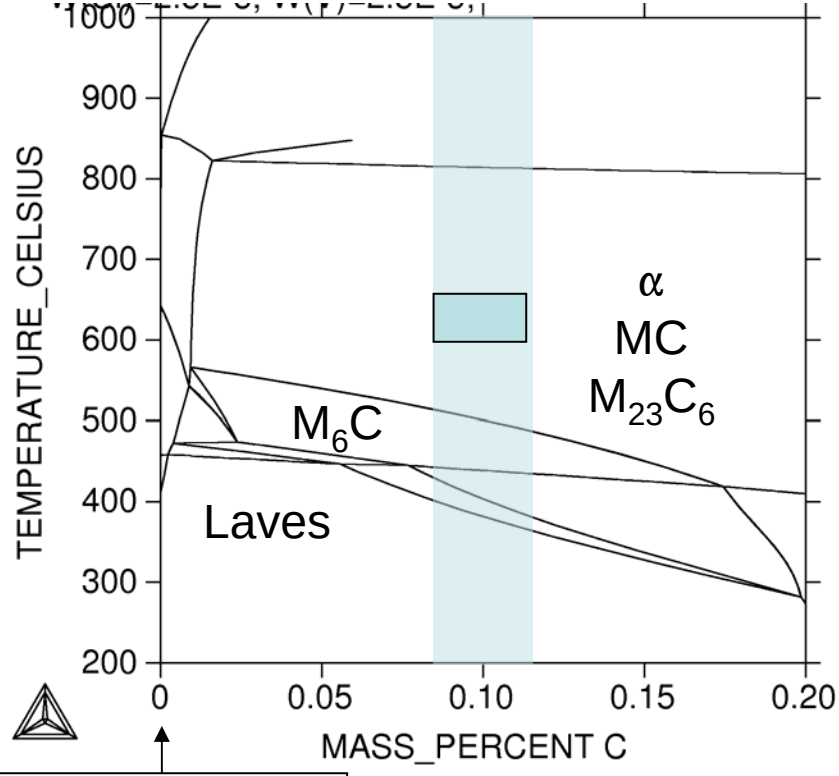
HR52 vs P91

HR52



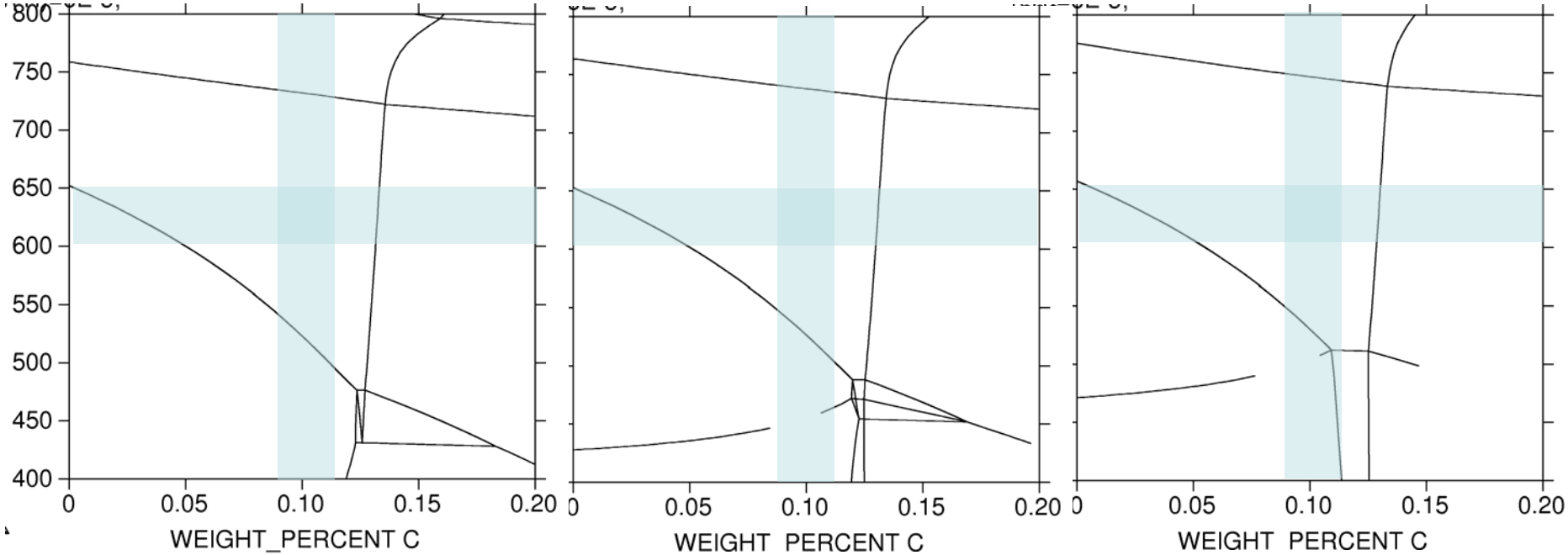
Fe-9Cr-3Cu-3Co-1Ni-0.7Mo-0.6Ti

P91



Fe-9Cr-0.5Mn-0.3Si 0.3Ni-1Mo-0.2V-0.08Nb

Effect of Cr on the equilibrium phases



HR52 (9%Cr)

HR53 (10.5%Cr)

HR54 (12%Cr)

Melting and Casting

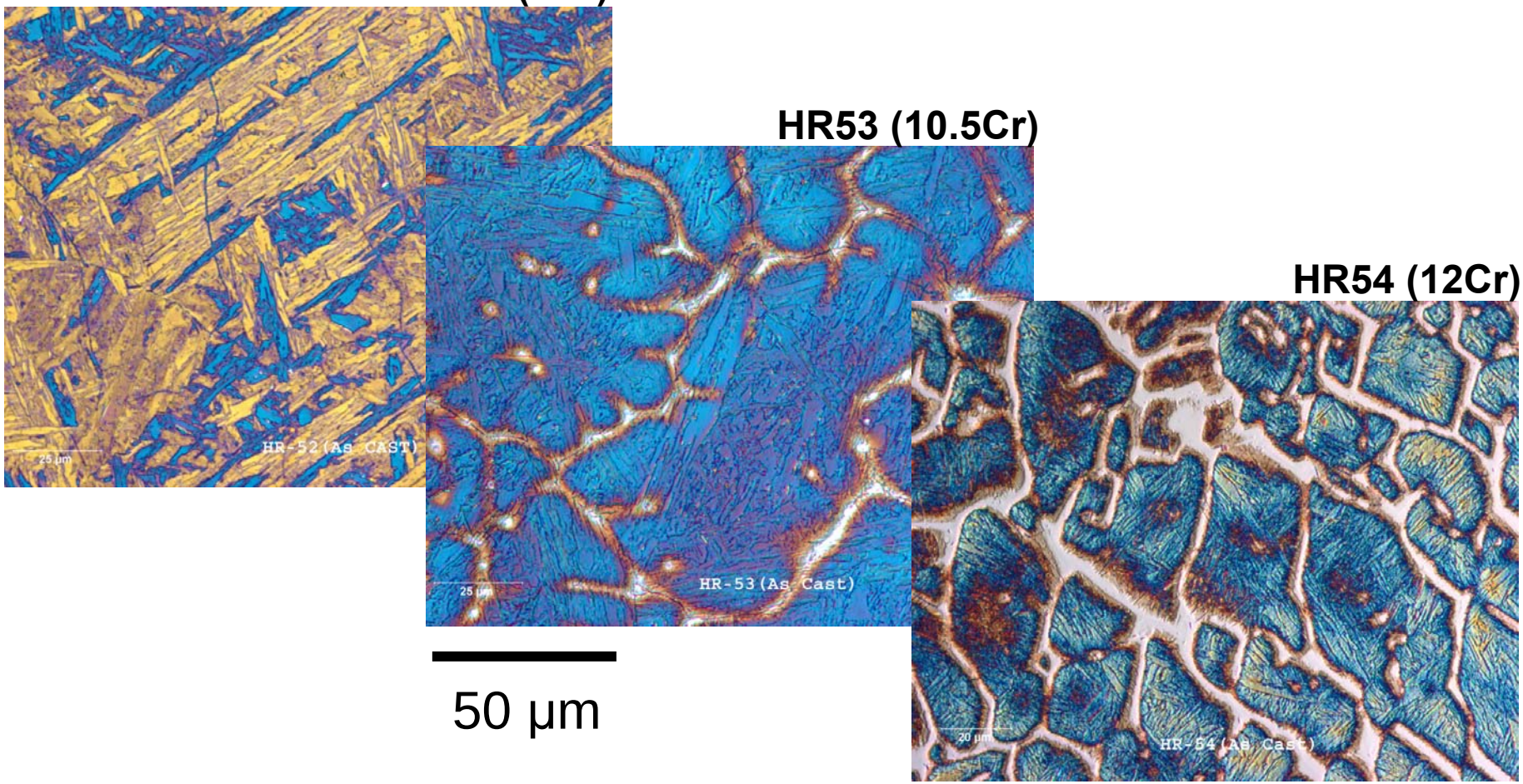
- Experimental steels were vacuum induction melted using elemental charge materials
- They were poured into ceramic coated, 2 in diameter graphite molds

Microstructure of steels in the as-cast condition

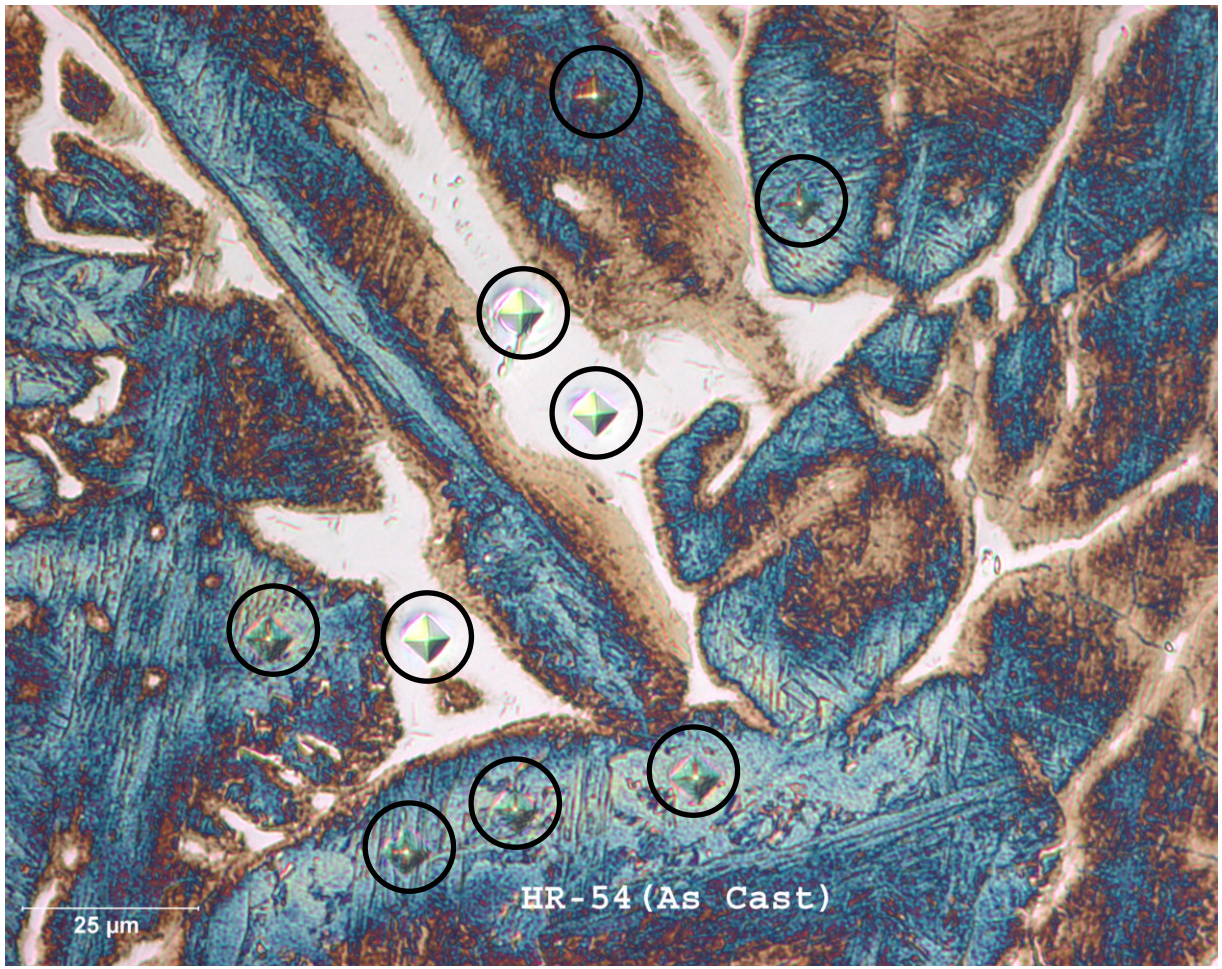
HR52 (9Cr)

HR53 (10.5Cr)

HR54 (12Cr)



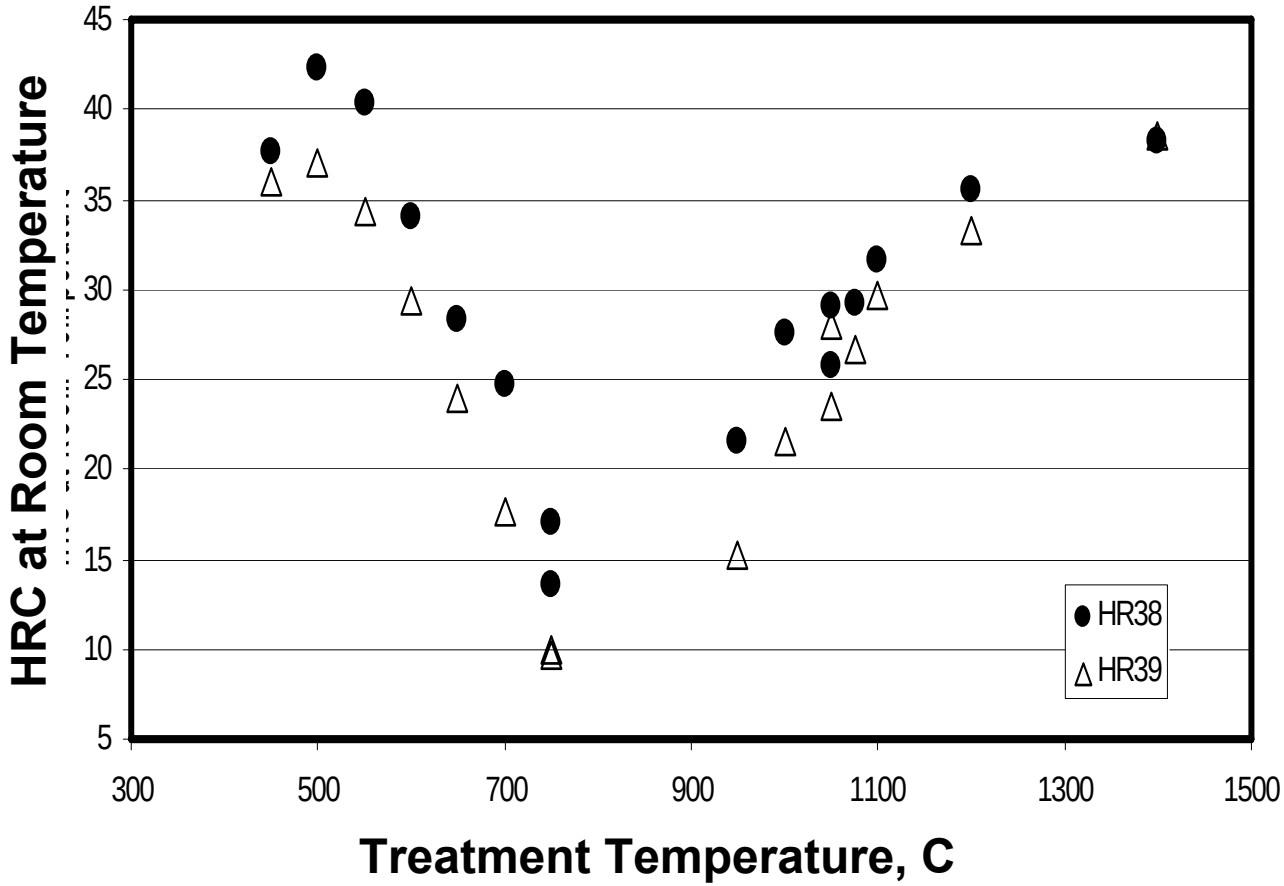
Martensite vs ferrite



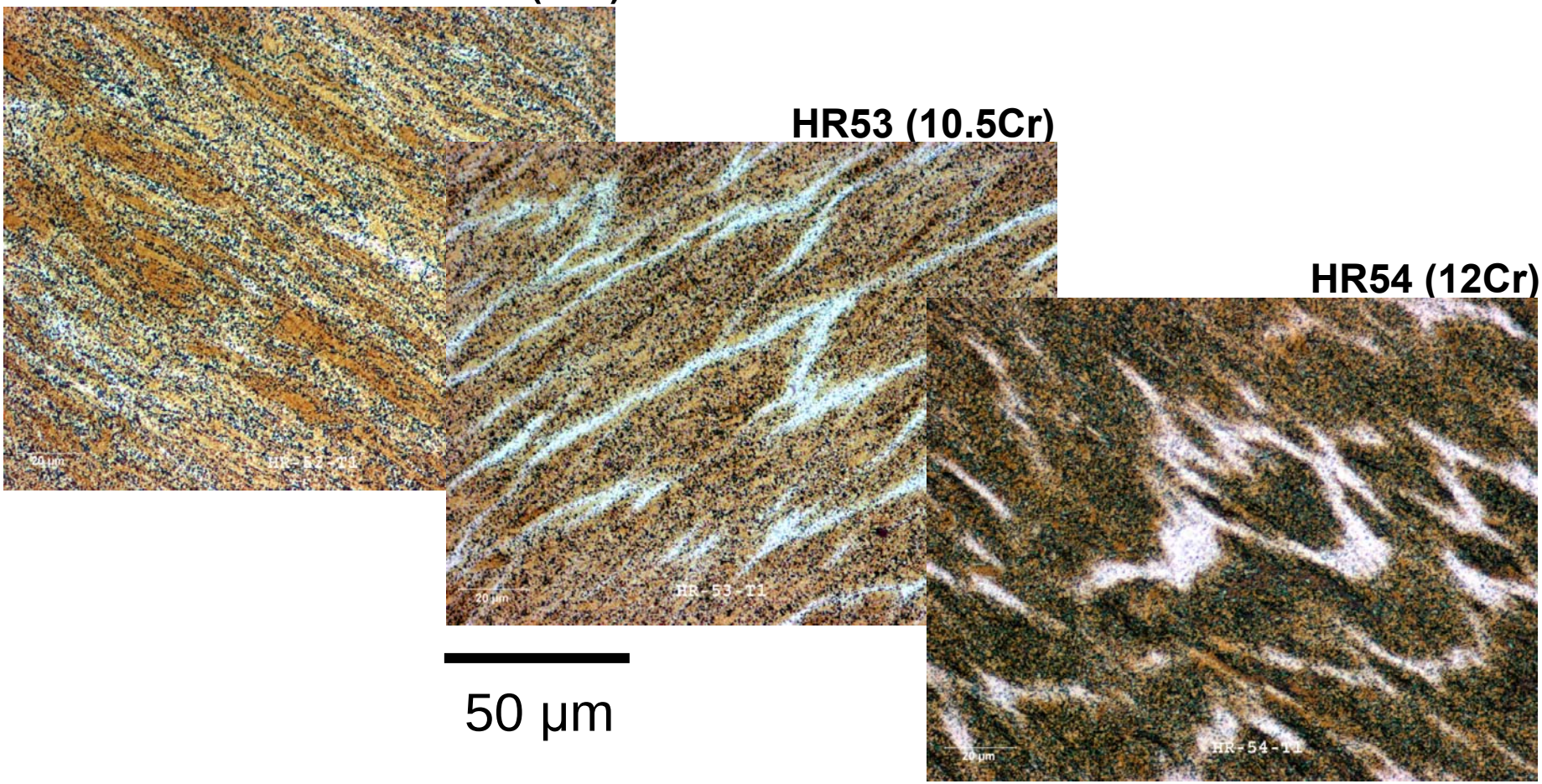
Thermomechanical Treatment

- Rolled at 750°C for 83% reduction in 14 passes
- Heat treated at 750°C for 1, 10, 100, and 1000 hours.

Choice of 750°C for heat treatment



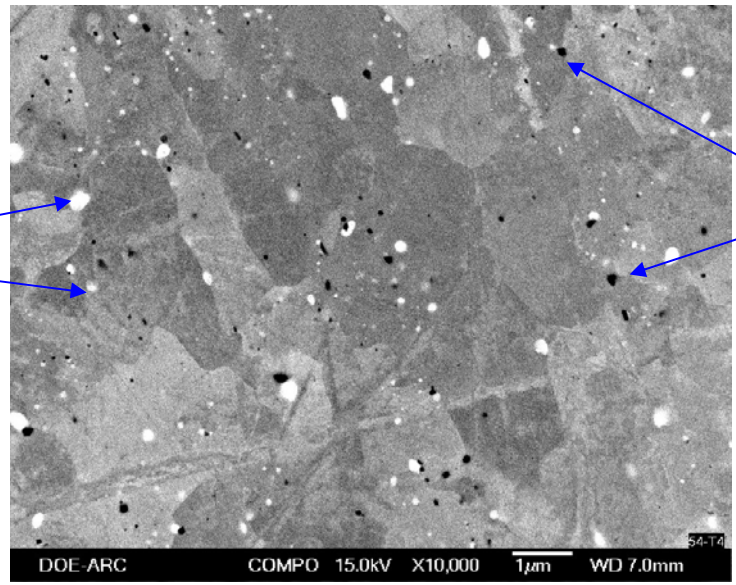
Microstructure of steels in the as-rolled condition



Microstructure Precipitates

Cu-rich

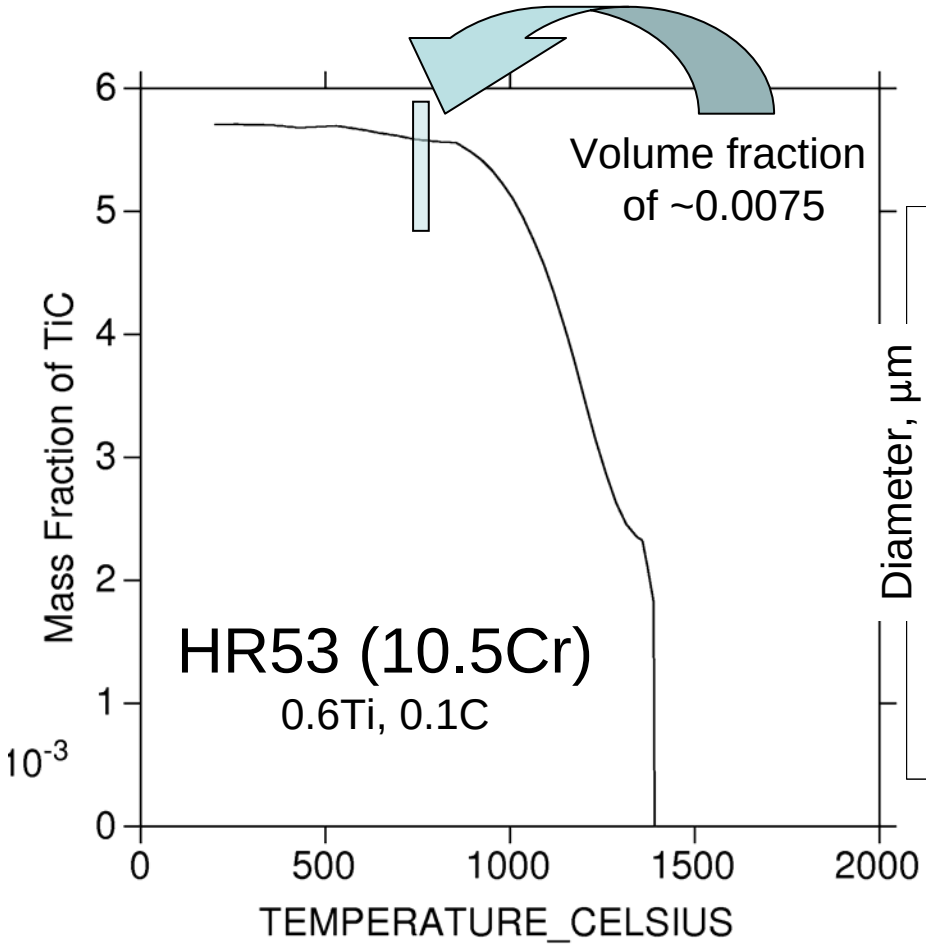
Mass%
95Cu-3.8Mo-0.7Co
-0.3Ni-0.2Fe

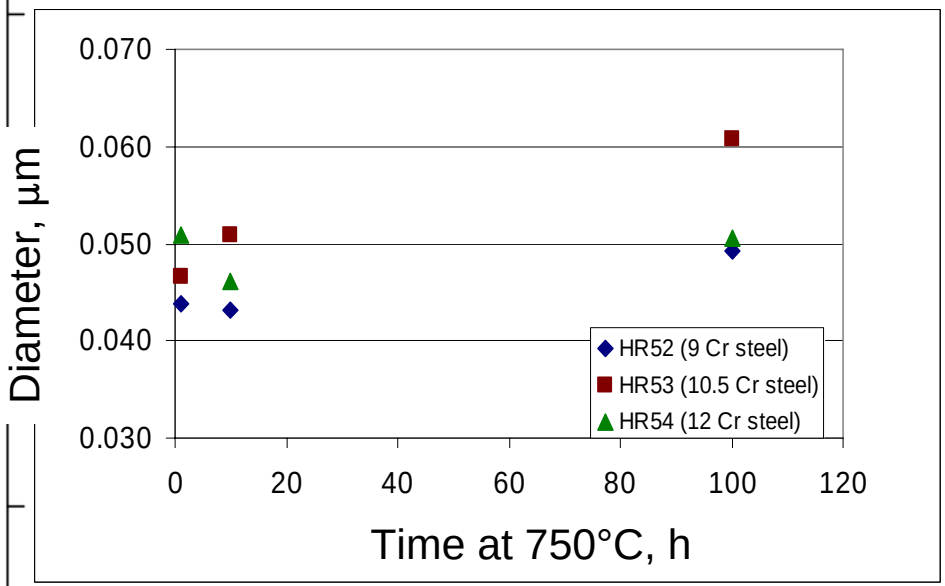


TiC

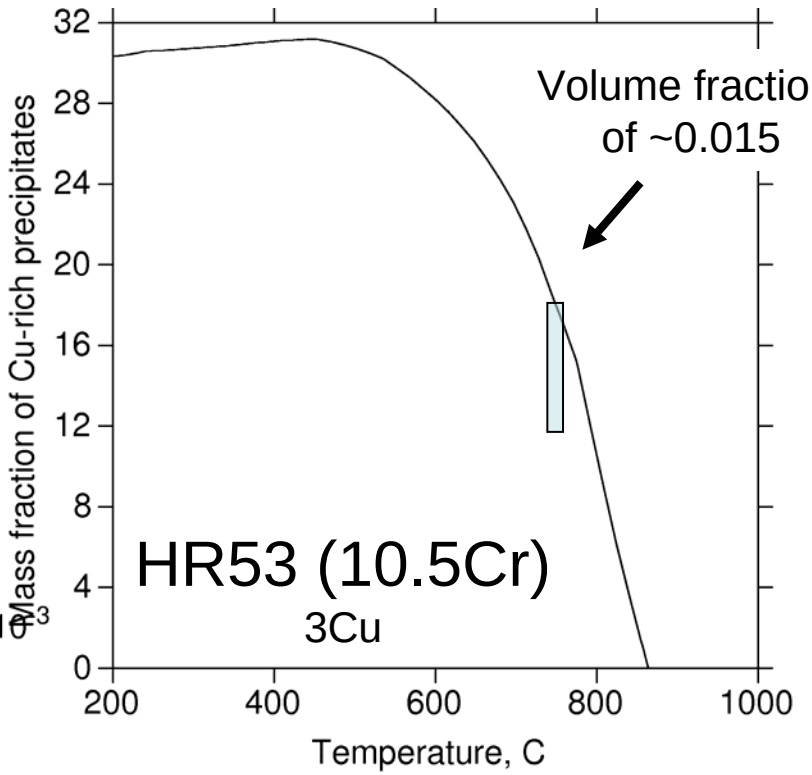
Mass%
82Ti-18C

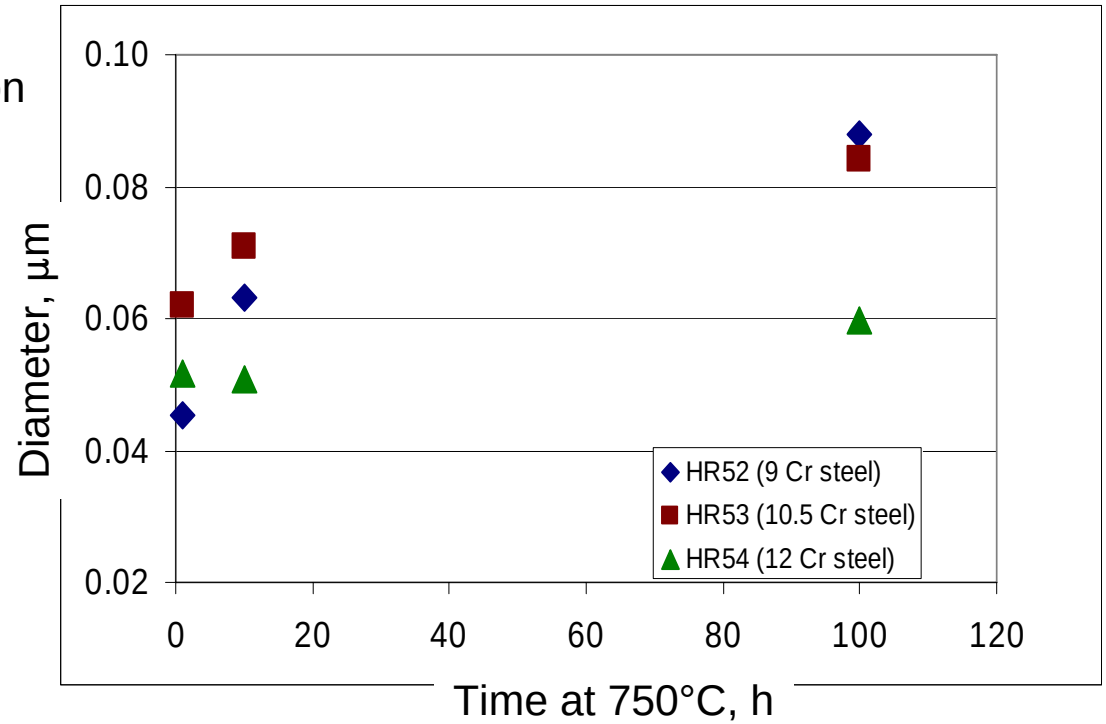
TiC Precipitates



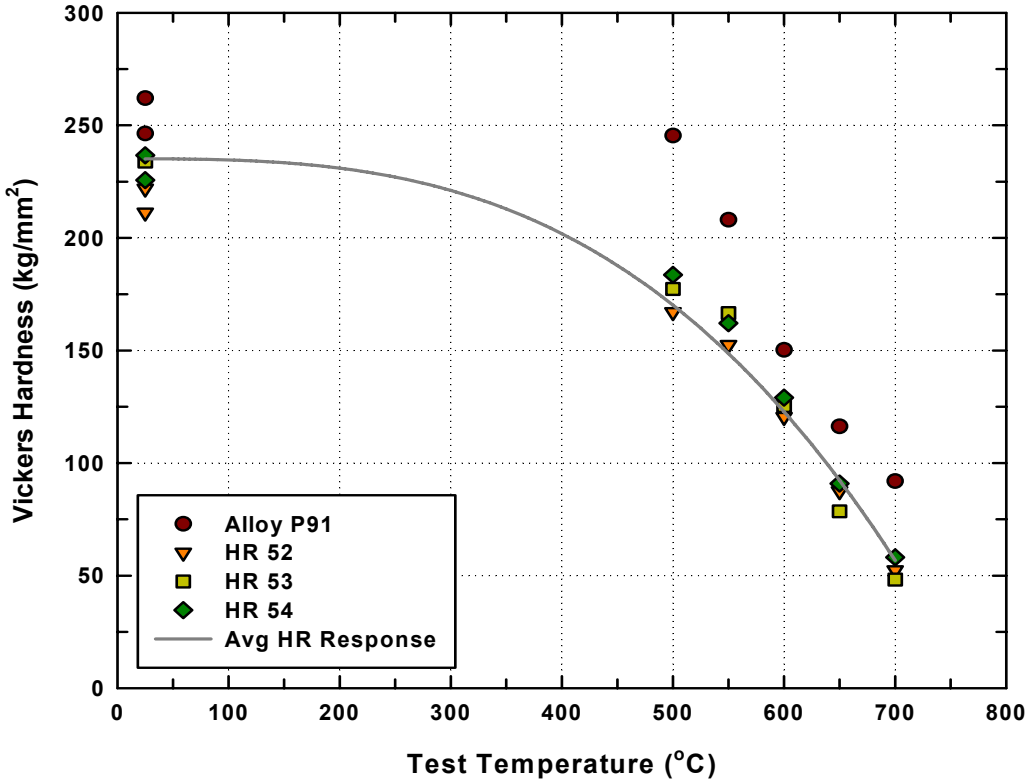


Cu-rich Precipitates





Hot Hardness Tests



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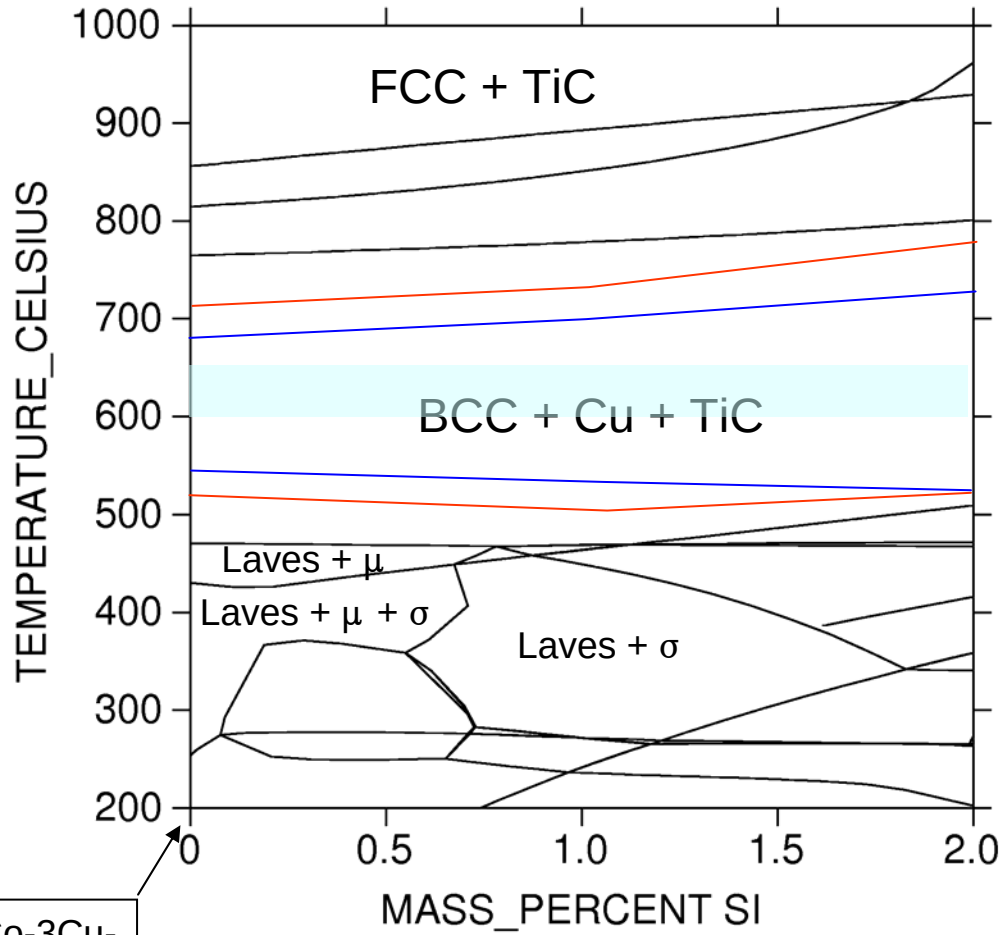
Effect of Mn and Si



1.0 Mn

Fe-9Cr-3Co-3Cu-0.7Mo-0.5Ti-0.1C

Summary

- Thermodynamic calculations predict equilibrium phases as bcc-Fe, TiC, and Cu-rich phase at the possible application temperature range of 600-650C for the experimental 9-12Cr steels.

Summary continued

- In both the as cast and rolled conditions, these steels are primarily martensitic with some ferrite.
- As the Cr level increases from 9 to 12 wt%, amount of delta ferrite in the matrix increases.

Summary continued

- Both TiC and Cu-rich precipitates provide strengthening.
- After up to 100h treatment at 750C, the TiC precipitates do not coarsen significantly. On the other hand, the Cu-rich precipitates coarsen at a faster rate.

Summary continued

- Effect of Si and Mn additions on the oxidation resistance and mechanical properties is being studied.